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## (54) PRODUCTION OF TABLET OR BRIQUETTE-FORMED DETERGENT COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a tablet or briquette-formed detergent composition having excellent solubility.

SOLUTION: The objective tablet or briquette-formed detergent composition having a bulk density of 1.0-2.0g/ml, is produced by mixing a detergent raw material containing a nonionic surfactant having a melting point of  $\leq 40^{\circ}\text{C}$ , an oilabsorbing agent for occluding the nonionic surfactant and a crystalline silicate as essential components, granulating the mixture to obtain detergent particles having an average particle diameter of 150-1,500 $\mu\text{m}$  and a bulk density of 0.6-1.2g/ml and tableting or briquetting the obtained detergent particles.

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CLAIMS

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[Claim(s)]

[Claim 1] Following (1) (2) And (3) The manufacture approach of the tablet mold which consists of a process, or a briquette mold cleaner constituent. Process (1) -- Process which mixes the detergent raw material which contains the oil absorption agent and the crystalline silicate for carrying out occlusion of the Nonion activator with a melting point of 40 degrees C or less and this Nonion activator as an indispensable component. Process (2) -- Process (1) The obtained mixture is corned and it is mean particle diameter. 150-1500 micrometers Bulk density Process which obtains a 0.6 - 1.2 g/ml detergent particle. process (3) -- process (2) the obtained detergent particle -- compressing -- bulk density 1.0-2.0g/ml it is -- process which obtains a tablet or a briquette.

[Claim 2] The manufacture approach of the tablet mold according to claim 1 whose oil absorption agents are a silica derivative and/or a spray drying particle, or a briquette mold cleaner constituent.

[Claim 3] a detergent raw material -- the following (a), (b) and (c) from -- the manufacture approach of the tablet mold according to claim 2 which it is in any which are chosen, or a briquette mold cleaner constituent. (a) Builder (a crystalline silicate) it contains -- 20 - 89 weight section, the silica derivative 1 - 20 weight sections, and the Nonion activator 10 - 60 weight sections (b) The mixture 75 of a builder (a crystalline silicate is included) / spray drying particle = 5 / 95 - 95/5 (weight ratio) - 95 weight sections, and the Nonion activator 5 - 25 weight sections (c) A builder (a crystalline silicate is included) / spray drying particle = the mixture 20 of 5 / 95 - 95/5 (weight ratio) - 89 weight sections, the silica derivative 1 - 20 weight sections, and the Nonion activator 10 - 60 weight sections [claim 4] Process (2) Process after mixing a surface lining agent further and carrying out the coat of the front face of a detergent particle by this surface lining agent to the back in between (3) The tablet mold of claim 1-3 given in any 1 term to perform, or the manufacture approach of a briquette mold cleaner constituent.

[Claim 5] It is the detergent particle 100 about a surface lining agent. As opposed to the weight section The manufacture approach of the tablet mold according to claim 4 which carries out 0.5-30 weight section mixing, or a briquette mold cleaner constituent.

[Claim 6] The tablet mold of claim 1-5 which contains a crystalline silicate one to 30% of the weight in [ all ] a constituent given in any 1 term, or the manufacture approach of a briquette mold cleaner constituent.

[Claim 7] Process (2) It is a mean diameter further the back. 100-1500 micrometers With a carbon number of six or less monochrome, polycarboxylic acid, or these salts Process after blending by the weight ratio to a detergent particle at a rate of [a carboxylic acid (salt)] / [detergent particle] = 1 / 99 - 30/70 and mixing with a detergent particle (3) The tablet mold of claim 1-3 given in any 1 term to perform, or the manufacture approach of a briquette mold cleaner constituent.

[Claim 8] After carrying out the coat of the front face of a detergent particle by the surface lining agent, it is a mean diameter further. 100-1500 micrometers With a carbon number of six or less monochrome, polycarboxylic acid, or these salts Process after blending by the weight ratio to the detergent particle behind a coat at a rate of [a carboxylic acid (salt)] / [detergent particle] = 1 / 99 - 30/70 and mixing with a coat detergent particle (3) The manufacture approach of the tablet mold according to claim 7 to perform or a briquette mold cleaner constituent.

[Claim 9] The manufacture approach of the tablet mold according to claim 7 or 8 monochrome, polycarboxylic acid, or these salts of whose are one sort or two sorts or more of mixture chosen from an acetic acid (salt), a succinic acid (salt), a maleic acid (salt), and a citric acid (salt), or a briquette mold cleaner constituent.

[Claim 10] The manufacture approach of claim 1-9 which a cleaning agent constituent is a briquette mold cleaner constituent, and is characterized by maximum length being [ of the perpendicular projection image of the briquette mold cleaner constituent concerned ] 10mm or less absolutely given in any 1 term.

[Claim 11] The manufacture approach of claim 1-9 which a cleaning agent constituent is a tablet mold cleaner constituent, and is characterized by maximum length being [ of the tablet mold cleaner constituent concerned ] 50mm or less absolutely given in any 1 term.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[The field of the invention to which invention belongs] This invention relates to the manufacture approach of the tablet mold excellent in the solubility which makes a nonionic surface active agent the main basis, or a briquette mold cleaner constituent.

[0002]

[Description of the Prior Art] Usually, as a gestalt of the cleaning agent currently used, there are two sorts, a liquefied type and a granular type. As for especially current, the powder-like thing is mainly used. However, powder may scatter at the time of use and the powdered cleaning agent had the fault of giving a user displeasure. In order to solve this problem, many attempts for tablet-izing a powder detergent conventionally are proposed.

[0003] For them, the tablet mold detergent which used the Nonion activator as the main washing surface active agent although the tablet mold detergent which blended the ionic surfactant as a main washing surface active agent was in use is also United States Patent specification 3231506th. A number and United States Patent specification 3247123rd A number and United States Patent specification 3331780th A number and United States Patent specification 3344076th It is known for the number etc.

[0004] there be no spilling of powder compared with a cleaning agent the aforementioned liquefied type and granular type, while there be an advantage of be easy to use, it have the reinforcement which can bear enough during handling and conveyance, and the property of dissolve promptly at the time of use be require, and if these tablet mold detergents generally raise moulding pressure and reinforcement of a tablet be make high, the fault that underwater solubility fall will produce them.

[0005] In order to conquer such a fault, the proposal of the former many has been made. Into them, the approach and carbonate which are made into porosity by performing heat-treatment after mixing and fabricating decomposition or volatile material, and solid acid are blended, and there are an approach of making generate carbon dioxide gas underwater and promoting the dissolution and approaches (JP, 44-17745, B, JP, 47-27208, B, etc.) which make it easy to blend the disintegrator widely used in the field of the chemical, and to collapse a tablet underwater.

[0006] However, it has set to these approaches, and a gap may not fully be practically satisfied, either, although to some extent underwater solubility improves. In the tablet which contained a surfactant like a detergent so much as the reason, since a surfactant hydrates underwater and it is extremely tintured with a viscous high property, it is possible that it becomes impossible that it is hard to advance water into the interior of a tablet, and a dissolution facilitatory effect is not fully demonstrated.

[0007] Considering as a briquette mold on the other hand in addition to the approach of using a cleaning agent constituent as a tablet mold is known. It is made to rotate so that a briquette mold cleaner constituent may blow mutually the roll which dug the pocket used as the mold of a briquette to prepare deep on the front face to a tablet being making tablet shaping by irregularity and it may be crowded, and is the thing which supplies a raw material for biting and crowding, compresses, and is obtained.

[0008] Therefore, since the shaping side of the roll which dug the mold of a briquette deep be a curved surface, it will be in the condition that the mold of a briquette do not close completely and the path of the air for the air omission of the raw material in compression be always secure for this reason, restoration nature and compressibility be high and a mold-goods internal structure have homogeneity and the advantage that it be dense and air cannot remain easily, as compared with a tablet mold detergent.

[0009] Some constituents of a briquette mold detergent are proposed until now (JP, 44-14681, A and WO9423010). However, these constituents were not enough examined about soluble improvement, although spilling of the powder of a powdered detergent was canceled, and solubility was not enough.

[0010]

[Means for Solving the Problem] The paste-like Nonion activator is made into the main basis, the detergent raw material containing a crystalline silicate is mixed, this mixture is corned to specific bulk density and particle size, and this invention persons came to complete a header and this invention for liquefied or the tablet mold or briquette mold cleaner constituent which was excellent in solubility the tab retching or by carrying out briquetting in the detergent granulation object obtained further being obtained, as a result of inquiring wholeheartedly.

[0011] That is, this invention is following (1). (2) And (3) The manufacture approach of the tablet mold which consists of a process, or a briquette mold cleaner constituent is offered. Process (1) -- Process which mixes the detergent raw material which contains the oil absorption agent and the crystalline silicate for carrying out occlusion of the Nonion activator with a melting point of 40 degrees C or less and this Nonion activator as an indispensable component. Process (2) -- Process (1) The obtained mixture is corned and it is mean particle diameter. 150-1500 micrometers Bulk density Process which obtains a 0.6 - 1.2 g/ml detergent particle. process (3) -- process (2) the obtained detergent particle -- compressing -- bulk density 1.0-2.0g/ml it is -- process which obtains a tablet or a briquette.

[0012] Moreover, it is as being shown in following 2-18 as instantiation of the desirable mode of this invention.

[0013] 2. Oil absorption agents are a silica derivative and/or a spray drying particle. The spray drying particle which the oil absorption agent as used in the field of this invention points out the porous particle which can carry out occlusion of the liquefied matter, is made to carry out spray drying of the slurry which consists of a detergent component and water especially, and is obtained, and/or a silica derivative are desirable.

[0014] 3. (a) of the following [ raw material / detergent ], (b) and (c) from -- it is in any which are chosen. (a) Builder (a crystalline silicate)

it contains -- 20 - 89 weight section, the silica derivative 1 - 20 weight sections, and the Nonion activator 10 - 60 weight sections (b) The mixture 75 of a builder (a crystalline silicate is included) / spray drying particle = 5 / 95 - 95/5 (weight ratio) - 95 weight sections, and the Nonion activator 5 - 25 weight sections (c) the mixture 20 of a builder (a crystalline silicate is included) / spray drying particle = 5 / 95 - 95/5 (weight ratio) - 89 weight sections, the silica derivative 1 - 20 weight sections, and the Nonion activator 10 - 60 weight sections -- here what has the following description comes out of a builder, a spray drying particle, and a silica derivative. - builder: -- a crystalline silicate, and the powder builders and at least 1 or more sorts of organic or inorganic spray drying particles: other than this -- the particle and silica derivative: which carried out spray drying of the water slurry containing at least one or more sorts of organic or inorganic builders -- a method of mercury penetration -- pore volume The oil absorption in 20-700m<sup>2</sup>/g and JIS K 5101 with 3/100g and a BET adsorption method 100-600cm<sup>3</sup>/100ml / 100g Silica derivative which it is above. [ specific surface area ]

[0015] 4. Process (2) Process after mixing a surface coating agent further and covering the front face of a detergent particle with this surface coating agent the back in between (3) It carries out.

[0016] 5. Set to the above 4 and it is a detergent particle about a surface coating agent. As opposed to the 100 weight sections 0.5-30 weight section mixing is carried out.

[0017] 6. Which manufacture approach of of said 1-5 which contain crystalline silicate one to 30% of the weight in [ all ] constituent.

[0018] 7. Process (2) It is a mean diameter further the back. 100-1000 micrometers Process after blending with a carbon number of six or less monochrome, polycarboxylic acid, or these salts by the weight ratio to a detergent particle at a rate of [a carboxylic acid (salt)] / [detergent particle] = 1 / 99 - 30/70 and mixing with a detergent particle (3) It carries out.

[0019] 8. After covering the front face of a detergent particle with a surface coating agent, it is a mean diameter further. 100-1000 micrometers Process after blending with a carbon number of six or less monochrome, polycarboxylic acid, or these salts by the weight ratio to the detergent particle after covering at a rate of [a carboxylic acid (salt)] / (covering detergent particle) = 1 / 99 - 30/70 and mixing with a covering detergent particle (3) Said 7 manufacture approaches to perform.

[0020] 9. Said 7 or 8 manufacture approaches monochrome, polycarboxylic acid, or these salts are kind or two sorts or more of mixture chosen from acetic acid (salt), succinic acid (salt), maleic acid (salt), and citric acid (salt).

[0021] 10. The Nonion activator is [ the number of ethyleneoxide average addition mols of the alcohol of the 1st class or the 2nd class ] polyoxyethylene alkyl ether of 5-15 in the straight chain or branched chain of carbon numbers 10-20.

[0022] 11. Use one sort or two sorts or more of mixture chosen from sodium tripolyphosphate, a sodium carbonate, an aluminosilicate, citrate, polyacrylate, and a polyethylene glycol as builders other than a crystalline silicate.

[0023] 12. A spray drying particle is a particle which carried out spray drying of the water slurry containing one sort or two sorts or more of mixture chosen from sodium tripolyphosphate, a sodium carbonate, an aluminosilicate, citrate, polyacrylate, and a polyethylene glycol.

[0024] 13. A silica derivative is an amorphous aluminosilicate.

[0025] 14. The mean particle diameter of the primary particle of a surface coating agent is 10 micrometers. The mean particle diameter of the manufacture approach 15. primary particle of said 4, 5, or 8 publications which are the followings is 10 micrometers. The manufacture approach of the above 16 that the following surface coating agents are one sort or two sorts or more of mixture chosen from silicate compounds, such as an aluminosilicate and an amorphous silica derivative.

[0026] 16. process (2) Mean particle diameter of the obtained Nonion detergent particle 250-800 μm it is .

[0027] 17. A cleaning agent constituent is a briquette mold cleaner constituent, and it is which manufacture approach of the perpendicular projection image of the briquette mold cleaner constituent concerned of said 1-16 whose maximum length is 10mm or less absolutely.

[0028] 18. A cleaning agent constituent is a tablet mold cleaner constituent, and it is which manufacture approach of the tablet mold cleaner constituent concerned of said 1-16 whose maximum length is 50mm or less absolutely.

[0029] The manufacture approach of the following this inventions is explained. [Process (1)] Process in the manufacture approach of this invention (1) It is the process which mixes the detergent raw material which contains the Nonion activator with a melting point of 40 degrees C or less, the oil absorption agent for carrying out occlusion of this Nonion activator, and a crystalline silicate as an indispensable component.

[0030] Process (1) Although especially the approach to the mixer of the combination component of a detergent raw material to teach is not limited in operation, when mixing a raw material by the batch process, after teaching a component with more desirable blending first among the builder of organic or inorganic powder, an oil absorption agent, a crystalline silicate, and an arbitration component to a mixer, the Nonion activator is added and especially the approach of mixing is desirable.

[0031] Moreover, process (1) Mixing and process (2) Although the equipment of continuous system can also perform a granulation, and a detergent raw material is mixed continuously in this case or mixing and a granulation are performed to coincidence, especially the supply approach of a detergent raw material is not limited. In this invention, when mixing and coming a detergent raw material continuously, all the other powder raw materials are beforehand mixed with the Nonion activator with the batch method, and the mixture may be continuously supplied to a granulation process. Moreover, as for the Nonion activator, also in either approach of a batch process and continuous system, spraying and supplying is desirable.

[0032] Process of this invention (1) Following equipment is mentioned as equipment used suitably. First, as equipment in the case of carrying out by the batch process, it is the following. (1) - (4) A thing is used suitably. (1) It is the mixer of the format which has a stirring shaft inside by the mixing chamber, attaches an impeller in this shaft, and mixes powder. For example, although there are a Henschel mixer [the product made from Mitsui Miike Chemically-modified Opportunity], a high speed mixer [the product made from Fukae Industry], vertical granulator [Powrex Make], etc., it is the mixer of the format which has a stirring shaft at the cylindrical core by the mixing chamber of a horizontal type preferably, attaches an impeller in this shaft, and mixes powder especially, for example, there are a REDIGE mixer [made in Matsusaka Research Institute] and a BUROSHIEA mixer [the product made from Pacific Ocean machine \*\*]. (2) There is a mixer of the format mixed when the mixing chamber which carried out the V character mold rotates, for example, a V type mixer, [the Fuji Paudal make]. (3) There is a mixer of the format mixed when the wing of the shape of a ribbon which formed the spiral within the container with which the semi-cylindrical shape was fixed rotates, for example, a ribbon mixer, [the Fuji Paudal make]. (4) There are a mixer of the format mixed by revolving around the sun while a screw rotates considering a shaft parallel to the wall of a container as a core along with a conical-like container, for example, a NAUTA mixer, [the Hosokawa Micron CORP. make], and an SV mixer [the product made from \*\*\*\* Van Tech].

[0033] Moreover, as equipment in case continuous system performs, it is following (1). - (3) A thing is used suitably. (1) Consisting of the main shaft equipped with the vertical-type cylinder equipped with fine-particles input port, and the mixed blade, a main shaft is supported

by up bearing and has, the continuous mixer [Powrex Make], for example, the flexo mix mold, of the structure which is free. (2) A raw material is thrown into the upper part of a disk with a stirring bottle, high-speed rotation of this disk is carried out, and there are the continuous mixer of the format mixed according to a shear operation, for example, a flow jet mixer, [the product made from \*\*\*\* Bow Tex], and a spiral bottle mixer [the product made from Pacific Ocean machine \*\*]. (3) It is the continuous system mixer of the format which has a stirring shaft inside by the mixing chamber, attaches an impeller in this shaft, and mixes powder. For example, there is a continuation Henschel mixer [the product made from Mitsui Miike Chemically-modified Opportunity]. Furthermore, equipments, such as a high speed mixer [the product made from Fukae Industry] and vertical granulator [Powrex Make], may be used as an interlocking device. It is the thing of continuous system by the mixer of the format which has a stirring shaft at the cylindrical core by the mixing chamber of a horizontal type preferably, attaches an impeller in this shaft, and mixes powder, for example, there are a REDIGE mixer [made in Matsusaka Research Institute] and a BUROSHIEA mixer [the product made from Pacific Ocean machine \*\*].

[0034] [Process (2)] Process in the manufacture approach of this invention (2) Process (1) The obtained mixture is corned and it is mean particle diameter. 150-1500 micrometers Bulk density It is the process which obtains the 0.6-1.2g /ml ] Nonion detergent particle.

[0035] Process of this invention (2) The granulation approach of the detergent generally known can be used for the granulation approach which can be set, and an extrusion granulating machine, a fluidized-bed-granulation machine, tumbling granulator, stirring tumbling granulator, etc. are suitably used as common equipment used at this time. As an example of a fluidized-bed-granulation machine, spiral flow [the Freund Industrial make], a multiprocessor [Powrex Make], etc. are mentioned. As an example of tumbling granulator, the Malmo riser [the Fuji Paudal make], CF granulator [the Freund Industrial make], etc. are mentioned. As an example of stirring tumbling granulator, a Henschel mixer [the product made from Mitsui Miike Chemically-modified Opportunity], a high speed mixer [the product made from Fukae Industry], vertical granulator [Powrex Make], etc. are mentioned.

[0036] In addition, process of this invention (2) As granulator used, it has the stirring shaft equipped with the impeller at the internal core, and in case an impeller rotates, the stirring mold mixer which is the structure which forms path clearance between an impeller and a container wall can also be used. As a stirring mold mixer which has such structure For example, the product made from Henschel mixer [Mitsui Miike Chemically-modified Opportunity, a high speed mixer [the product made from Fukae Industry], There are equipments, such as vertical granulator [Powrex Make]. It is the mixer of the format which has a stirring shaft at the cylindrical core by the mixing chamber of a horizontal type preferably, attaches an impeller in this shaft, and mixes powder especially, for example, is a REDIGE mixer (it can corn by Matsusaka Research Institute] and the BUROSHIEA mixer [the product made from Pacific Ocean machine \*\*].).

[0037] process (2) \*\*\*\* -- although any of the above equipments may be used -- process (2) the detergent particle obtained -- mean particle diameter 150-1500 micrometers desirable -- 150-1000 micrometers further -- desirable -- 250-800 mum And bulk density 0.6-1.2g/ml -- desirable -- It is necessary to be 0.7-1.0g/ml. When mean particle diameter and bulk density use the detergent granulation object which separated from such range, effectiveness of this invention cannot be acquired.

[0038] [Process (3)] Process in the manufacture approach of this invention (3) Process (2) The obtained detergent particle is compressed into 1.0-2.0g /ml ] bulk density, and the volume is the process which obtains 1.0cm three or more tablets at least.

[0039] Process of this invention (3) As equipment for compression used, if a tablet or a briquette is obtained, it will not be limited, but a well-known tableting machine and a briquetting machine can be used. a tableting machine -- the inside of a mortar -- a granulation object -- being filled up -- lower -- a pestle -- the upper -- it is equipment compressed and fabricated between pestles. a tableting machine -- one mortar -- while a mortar is embedded at equal intervals on the periphery of the single-engined tableting machine which the pestle of a vertical lot moves up and down and compresses inside, and the turntable which rotates horizontally and a turntable rotates, the rotary tableting machine with which a series of actuation of restoration, compression, and discharge is performed continuously is. A briquetting machine is equipment which supplies a granulation object between the rolls which two rolls with which the pocket used as the matrix of the compression object for which it asks on a periphery is minced eat away mutually, and rotate by this \*\* in the kitchen, and is pressed continuously.

[0040] It sets to this invention and is a process (2). It is a process (3) behind. As an advantage which compresses, the Nonion activator or a binder oozes out from a detergent granulation object at the time of compression. This serves as a moderate binder of a detergent and can give the outstanding affinity, i.e., reinforcement. Moreover, the form of a detergent granulation object is maintained at the time of compression, and the property which was excellent also in solubility is shown in an underwater collapsibility pan. However, when it compresses, without using the detergent particle which corned or bulk density compresses using a 0.6g /ml ] or less detergent particle, the Nonion activator or a binder will spread round the whole compression object, and will have very strong affinity. That is, it leads to a soluble fall at the collapsibility pan to water.

[0041]

[Embodiment of the Invention] Next, the detergent raw material used for the manufacture approach of the tablet mold of this invention or a briquette mold cleaner constituent is explained.

[0042] In this invention, the Nonion activator with a melting point of 40 degrees C or less, the oil absorption agent for carrying out occlusion of this Nonion activator, and a crystalline silicate are contained in a detergent raw material as indispensable, and can blend the usual tablet mold or the arbitration component of a briquette mold cleaner constituent with it except these. As an especially desirable detergent raw material, they are the following (a). - (c) What is shown is mentioned. (a) A builder (a crystalline silicate is included) 20 - 89 weight sections, the silica derivative 1 - 20 weight sections, and the Nonion activator 10 - 60 weight sections (It is hereafter called a detergent raw material (a)) (b) A builder (a crystalline silicate is included) / spray drying particle = [ The mixture 75 - 95 weight sections, and the Nonion activator 5 - 25 weight sections of 5 / 95 - 95/5 (weight ratio) ] (It is hereafter called a detergent raw material (b)) (c) A builder (a crystalline silicate is included) / spray drying particle = [ The mixture 20 of 5 / 95 - 95/5 (weight ratio) - 89 weight sections, ] The silica derivative 1 - 20 weight sections, the Nonion activator 10 - 60 weight sections (henceforth a detergent raw material (c)) however the builder that is an oil absorption agent, a spray drying particle, and a silica derivative have the following description. - builder: -- a powder builder and at least 1 sort of organic or inorganic spray drying particle: -- the particle and silica derivative: which carried out spray drying of the water slurry containing at least one sort of organic or inorganic builders -- a method of mercury penetration -- pore volume 100-600cm<sup>3</sup>/100g a BET adsorption method -- specific surface area -- oil absorption of 20-700m<sup>2</sup>/5101 Detergent raw material (c) of the silica derivative above which are 100ml / 100g or more (d) in -- the purpose using a spray drying particle [ g and JIS K5101 ] (1) Control of bulk density, and (2) It is improvement in a builder's oil absorption.

[0043] A spray drying particle is obtained by drying the aquosity slurry of an organic or inorganic builder by the well-known spray drying method. Organic [ in that case ] or an inorganic builder is preferably blended 70% of the weight or more 50% of the weight or more among

a spray drying particle. The moisture of an aqueous slurry has 30 - 80 desirable % of the weight.

[0044] Although one sort or two sorts or more of anions, a cation, or the Nonion activator can be blended into a spray drying particle if needed, since the oil absorption capacity of a spray drying particle will decline if it blends 10% of the weight or more, it is not [ in / manufacture of this spray drying particle ] desirable. Moreover, other additives may be added 5 or less % of the weight. As other additives, binders, such as fluorescent dye, an anti-oxidant, and a carboxymethyl-cellulose salt, etc. are mentioned here.

[0045] Among the builders used for a spray drying particle, as an organic builder, citrate, polyacrylate, a polyethylene glycol, etc. are desirable, as an inorganic builder, sodium tripolyphosphate, a sodium carbonate, an aluminosilicate, etc. are desirable, and the permutite currently generally especially used for the detergent in this invention is desirable.

[0046] moreover, mean particle diameter of a spray drying particle 100-600 micrometers desirable -- further -- desirable -- 150-400  $\mu\text{m}$  it is . This mean particle diameter is measured using the standard sieve of JIS Z 8801 from the weight fraction by the size of the mesh after making it vibrate for 5 minutes.

[0047] Even if it carries out spray drying of the porous builder particle and is obtained, by carrying out spray drying, irregularity is formed in a front face, and the spray drying particle as an oil absorption agent concerning this invention chooses a builder who becomes porosity, and may be manufactured.

[0048] moreover, detergent raw material (b) in this invention (c) in -- organic or inorganic a powder builder (a crystalline silicate is included) and a spray drying particle -- a weight ratio -- a (builder) / (spray drying particle) = 5 / 95 - 95/5 -- desirable -- 20 / 80 - 90/10 -- 60 / 40 - 90/10 come out comparatively still more preferably, and it is used.

[0049] Next, among the oil absorption agents used by this invention, since a silica derivative shows the oil absorption ability pointed out the thing of the inorganic compound containing a silica and the amorphous thing excelled [ ability ] in this invention especially, it is desirable. As description, the pore volume in a method of mercury penetration 100 ml / thing 100g or more has [ the specific surface area in 100 to 600  $\text{cm}^3/100\text{g}$ , and a BET adsorption method ] the desirable oil absorption in 20-700  $\text{m}^2/\text{g}$  and JIS K 5101. This oil absorption shows the amount of the linseed oil absorbed by the silica derivative based on the approach indicated by JIS K 5101. Moreover, the mean particle diameter of a silica derivative is 0.5-500 micrometers as floc. It is 1-200 micrometers desirable still more preferably. This mean diameter is measured by the same approach as the above-mentioned builder's case.

[0050] As this silica derivative, the compost which contains aluminum 2O<sub>3</sub>, 2M<sub>2</sub>O (M is alkali metal here), MeO (Me is alkaline earth metal here), etc. as the 2nd component is good. Moreover, not only two elements but things, such as three elements and four elements, are used suitably. Specifically, they are the following (i). - (iii) The matter is illustrated. (i) As what uses a silica as a principal component, it is Carplex of the nip seal NS and nip seal NA-R made from TOKUSHIRU NR and PR by Tokuyama Soda Co., Ltd., AL-1, and Japanese Silica, the nip seal ES, Degussa AG SIPERNAT 22, SIPERNAT 50, DUROSIL, ZEOSIL 45 by the South Korean Buddha chemistry company, TIXOSIL 38, and the product made from Shionogi Pharmaceuticals. 100 is mentioned. (ii) As what uses a calcium silicate as a principal component, it is Huber HUBERSORB (trademark)600. It is mentioned. (iii) As what uses an aluminosilicate as a principal component, Degussa AG AluminiumSilicate P820 and TIXOLEX 25 by the South Korean Buddha chemistry company are mentioned. Especially as what uses the aluminosilicate of the above (iii) as a principal component, what is shown by the following general formulas is desirable. Moreover, these things have the description of having ion-exchange ability.

[0051] (1)  $x(\text{M}_2\text{O})$ , aluminum 2O<sub>3</sub>, and  $y(\text{SiO}_2) \cdot w(\text{H}_2\text{O})$  (M in a formula expresses alkali metal, such as sodium and a potassium, and x, and y and w express the number of mols of each component in the following range of number.) 0.2 Positive-Number (2)  $X(\text{MeO})$ , Y (M<sub>2</sub>O), Aluminum 2O<sub>3</sub>, Z (SiO<sub>2</sub>), and W of Arbitration Containing  $\leq X \leq 2.00.5 \leq Y \leq 10.0W:0$  (H<sub>2</sub>O) (Me in Formula -- Calcium -- Alkaline earth metal, such as magnesium, is expressed and it is M. Expressing alkali metal, such as sodium and a potassium, x, and y, z and w express the number of mols of each component in the following range of number.  $0.001 \leq x \leq 0.10.2 \leq y \leq 2.00.5$  In positive-number this invention of the arbitration containing  $\leq z \leq 10.0w:0$ , an especially amorphous aluminosilicate is desirable as a silica derivative.

[0052] In addition, little concomitant use of the compound in which oil absorption ability other than the following silica derivatives is shown may be carried out. 1) Flow light by calcium silicate Tokuyama Soda Co., Ltd. R is mentioned. 2) The cull light KT made from Calcium-carbonate Shiroishi Industry is mentioned. 3) Magnesium-carbonate TT by magnesium-carbonate Tokuyama Soda Co., Ltd. is mentioned. 4) The pearlite 4159 by pearlite (pearlite) Dicalite ORIENT CORP. is mentioned.

[0053] In addition, as a silica derivative of this invention, since clay matter like a smectite shows the inclination to reduce the solubility of a tablet or a briquette, it is not desirable.

[0054] The following is illustrated as a builder who can use it for manufacture of the Nonion detergent particle concerning this invention. In this invention, a crystalline silicate is treated as a builder. Moreover, a powder builder organic [ other ] or inorganic means the matter which can be dealt with as powder in the following builder. Moreover, the builder and water among organic [ these ] or inorganic builders which can be hydrated may be mixed, and you may use as hydrated salt. Moreover, it may be the same as the builder who used for manufacture of the above-mentioned spray drying particle.

[0055] As an inorganic builder, the following aluminosilicates besides phosphate (alkali-metal salts, such as sodium and a potassium), such as neutral salt, such as alkaline salts, such as an amorphous sodium silicate which is illustrated by a sodium carbonate, potassium carbonate, sodium bicarbonate, a sodium sulfite, sodium sesquicarbonate, JIS No. 1, No. 2, and No. 3, and a sodium sulfate, orthophosphate, a pyrophosphate, tripolyphosphate, a metaphosphate, a hexametaphosphoric acid salt, and a phytic acid salt, can also be mentioned.

[0056] No.1 Crystalline aluminosilicate  $x'(\text{M}_2\text{O})$ , aluminum 2O<sub>3</sub>, and  $y'(\text{SiO}_2) \cdot w'$  shown by the degree type (H<sub>2</sub>O) (among a formula) M alkali-metal atoms, such as sodium and a potassium, x', y', and w -- ' -- the mol of each component -- a number -- expressing -- general --  $0.7 \leq x' \leq 1.5$ ,  $0.8 \leq y' \leq 6$ , w' are the constants of arbitration. In these, what is shown especially by the following general formula is desirable. Na<sub>2</sub>O-aluminum 2O<sub>3</sub>, ySiO<sub>2</sub>, and wH<sub>2</sub>O (in y, 1.8-3.0 and w express the number of 1-6 among a formula.).

[0057] No.2 Amorphous aluminosilicate x, aluminum 2O<sub>3</sub>, and y (SiO<sub>2</sub>)  $\cdot w$  shown by the degree type (H<sub>2</sub>O) (M expresses sodium and/or a potassium atom among a formula, and x, and y and w express the number of mols of each component in the following range of number.) 0.7 The positive number of the arbitration containing  $\leq x \leq 1.21.6 \leq y \leq 2.8w:0$ .

[0058] No.3 Amorphous aluminosilicate x, aluminum 2O<sub>3</sub>, y (SiO<sub>2</sub>), z (P<sub>2</sub>O<sub>5</sub>), and w shown by the degree type (H<sub>2</sub>O) (the number of mols of each component which M has in x in sodium or a potassium atom among a formula, and y, z, and w have in the following range of number is expressed.)  $0.20 \leq x \leq 1.100.20$  Integer of the arbitration containing  $\leq y \leq 4.000.001 \leq z \leq 0.80w:0$ .

[0059] In these inorganic builders, it is sodium tripolyphosphate, a sodium carbonate, an aluminosilicate, and 100 (CaCO<sub>3</sub> mg/g). The silicate compound which has the above ion-exchange ability is more desirable.



[0060] Moreover, the following matter is illustrated as an organic builder.

[0061] 1) Ethane -1, 1-diphosphonic acid, ethane -1, 2-triphosphonic acid, Ethane-1-hydroxy - 1 and 1-diphosphonic acid and its derivative, Ethane hydroxy - 1, 1, 2-triphosphonic acid, ethane -1, 2-dicarboxy - 1, 2-diphosphonic acid, Salt 2 of phosphonic acid, such as methane hydroxy phosphonic acid 2-phosphono butane -1, 2-dicarboxylic acid, 1-phosphono butane - Salt 3 of phosphono carboxylic acids, such as 2, 3, 4-tricarboxylic acid, and alpha-methyl phosphono succinic acid Aspartic acid, Salt 4 of amino acid, such as glutamic acid A nitrilotriacetic acid salt, an ethylenediaminetetraacetic acid salt, Amino poly acetate 5, such as diethylenediamine 5 acetate Polyacrylic acid, Pori aconitic acid, the Pori itaconic acid, the Pori citraconic acid, the Pori fumaric acid, A polymer lane acid, the poly meta contest acid, a Polly alpha-hydroxy acrylic acid, A polyvinyl phosphonic acid, sulfonation polymer lane acid, and maleic-anhydride-diisobutylene copolymer, A maleic-anhydride-styrene copolymer, a maleic-anhydride-methyl-vinyl-ether copolymer, A maleic-anhydride-ethylene copolymer, a maleic-anhydride-ethylene crosslink copolymer, A maleic-anhydride-vinyl acetate copolymer, a maleic-anhydride-acrylonitrile copolymer, A maleic-anhydride-acrylic ester copolymer, a maleic-anhydride-butadiene copolymer, A maleic-anhydride-isoprene copolymer, a maleic anhydride and the Polly beta-keto carboxylic acid guided from a carbon monoxide, An itaconic acid, an ethylene copolymer, an itaconic-acid-acconitic acid copolymer, An itaconic-acid-maleic-acid copolymer, an itaconic-acid-acrylic-acid copolymer, A malonic-acid-methylene copolymer, an itaconic-acid-fumaric-acid copolymer, an ethylene glycol-ethylene terephthalate copolymer, A vinyl-pyrrolidone-vinyl acetate copolymer, 1-butene - 2, 3, a 4-tricarboxylic acid-itaconic-acid-acrylic-acid copolymer, The polyester poly aldehyde carboxylic acid which has the fourth ammonium, Cis--isomer [ of an epoxy succinic acid ], Pori [N, and N-screw (carboxymethyl) acrylamide], Pori (hydroxy acid), a DEMBUN succinic acid, a maleic acid, or terephthalic-acid ester, Starch phosphoric ester, dicarboxy starch, dicarboxy methyl starch, Polyelectrolytes 6, such as carboxyl methyl cellulose and succinate Polyethylene glycol, Polyvinyl alcohol, a polyvinyl pyrrolidone, a carboxymethyl cellulose, Non-dissociating giant molecules 7, such as cold-water fusibility urethane-ized polyvinyl alcohol Diglycolic acid, Oxy-disuccinic acid, carboxymethyl malic acid, cyclopentane - 1, 2, 3, 4-tetracarboxylic acid, Tetrahydrofuran - 1, 2, 3, 4-tetracarboxylic acid, tetrahydrofuran - 2, 2, 5, and 5-tetracarboxylic acid, Carboxymethyl ghosts, such as a citric acid, a lactic acid, a tartaric acid, cane sugar, a lactose, and a raffinose, The carboxymethyl ghost of pentaerythritol, the carboxymethyl ghost of a gluconic acid, A condensate with polyhydric alcohol or a saccharide, a maleic anhydride, or a succinic anhydride, A condensate with hydroxy acid, a maleic anhydride, or a succinic anhydride, Benzene polycarboxylic acid, ethane which are represented with a merit acid - 1, 1, 2, and 2-tetracarboxylic acid, Ethene - 1, 1, 2, and 2-tetracarboxylic acid, butane - 1, 2, 3, 4-tetracarboxylic acid, Propane - 1, 2, 3-tricarboxylic acid, butane -1, 4-dicarboxylic acid, Oxalic acid, a sulfo succinic acid, Deccan -1, 10-dicarboxylic acid, sulfotricarbaric acid, a sulfo itaconic acid, a malic acid, oxy-disuccinic acid, a gluconic acid, CMOS, and builder M etc. -- an organic-acid salt -- in the organic builder of these, citrate, polyacrylate, and a polyethylene glycol are more desirable. Especially a desirable thing is citric-acid 3 sodium, sodium polyacrylate, and molecular weight 4000-20000. It is a polyethylene glycol.

[0062] Next, although especially the Nonion activator used by this invention is not limited, the melting point must be liquefied or the thing which presents the shape of a paste in 40 degrees C or less, i.e., 40 degrees C. The Nonion activator 40 degrees C or more serves as a binder between the grain children who put a pressure at the time of the tab retching or briquetting with the powerful melting point, and solubility falls remarkably.

[0063] As an example of the Nonion activator, polyoxyethylene alkyl ether, Polyoxyethylene alkyl phenyl ether, polyoxyethylene sorbitan fatty acid ester, Polyoxyethylene sorbitol fatty acid ester, polyethylene glycol fatty acid ester, Polyoxyethylene polyoxypropylene alkyl ether, polyoxyethylene castor oil, Polyoxyethylene hydrogenated castor oil, polyoxyethylene alkylamine, a glycerine fatty acid ester, a higher-fatty-acid alkanol amide, alkyl glycoside, an alkylamine oxide, etc. are mentioned.

[0064] above all -- as the main Nonion activator -- carbon numbers 10-20 -- desirable -- 10-15 -- further -- desirable -- 5-15 ethyleneoxide average addition mols of the alcohol of the straight chain of 12-14 or branched chain, the 1st class, or the 2nd class -- it is preferably desirable 6-12, and to use the polyoxyethylene alkyl ether of 6-10 still more preferably. Moreover, although this polyoxyethylene alkyl ether generally contains the alkyl ether of the number of ethyleneoxide low addition mols so much, it is desirable for a 0-3-mol addition product to use 25 or less % of the weight of a thing preferably 35 or less % of the weight.

[0065] The loadings of the Nonion activator change with detergent raw materials. Namely, detergent raw material in this invention (a) (c) The loadings of the Nonion activator contained are 10 - 25 % of the weight preferably five to 25% of the weight. Detergent raw material (a) Or (c) When using and manufacturing the Nonion detergent particle, at less than 5 % of the weight, the Nonion activator has too low active component concentration, and it is not desirable. On the other hand, if the Nonion activator exceeds 25 % of the weight, powder physical properties, especially a fluidity fall and are not desirable. Moreover, detergent raw material in this invention (b) (d) The loadings of the Nonion activator contained are 15 - 50 % of the weight preferably ten to 60% of the weight. Detergent raw material (b) Or (d) When using and manufacturing the Nonion detergent, the loadings of the Nonion activator can be increased by using porous oil absorption support, but if the Nonion activator exceeds 60 % of the weight even in such a case, powder physical properties, especially a fluidity fall and are not desirable.

[0066] Moreover, it is a process (1) in order to promote a granulation in this invention at the time of granulation. The time of mixing, or (2) of a process A binder may be added at the time of granulation and mixed addition may be carried out with a nonionic surface active agent. As a binder which can be used by this invention at the time of mixing or granulation, the Nonion nature matter, such as water-soluble polymer solutions, such as a carboxymethyl cellulose, a polyethylene glycol, and a polycarboxylic acid salt like sodium polyacrylate, polyoxyethylene alkyl ether, fatty-acid monoethanolamide, and fatty-acid diethanolamide, a fatty acid, a silicate-of-soda water solution, water, etc. can be mentioned. The loadings of a binder are the mixture of a detergent raw material, or the detergent particle 100 after granulation. 0.1 - 10 weight section is desirable to the weight section, and 0.5 - 5 weight section is especially desirable.

[0067] Crystalline silicate salt powder exists, after most has distributed inside the last detergent particle. It is desirable to have not exposed on the front face of the last detergent particle substantially, when preventing the washing degradation by amorphous-izing by contact for the moisture from the external world, and an alkali buffer capacity fall according to carbon dioxide gas etc. further. Moreover, it is desirable to distribute inside, also when controlling refractory-izing and insolubilization which involved in the component of the perimeter which starts after amorphous-izing. Hereafter, the crystalline silicate used for this invention is explained concretely. The crystalline silicate used for this invention shows 11 or more pH in dispersion liquid 0.1% of the weight, and shows the outstanding alkali ability. Moreover, alkali buffer capacity [ as / whose amount until it adds the hydrochloric acid of a decinormal in this solution further and pH is set to 10 pH of the solution after having performed stirring for 3 minutes after adding 0.1g of crystalline silicates to 1l. ion exchange water, and fully dissolving or distributing silicate is 11 or more, and is at least 3ml or more ] is shown. The crystalline silicate used for this invention has a crystalline and water-soluble property, and the aluminosilicate currently generally called the zeolite is distinguished.

[0068] as the crystalline silicate used for this invention -- alkali-metal silicate -- desirable -- especially --  $\text{SiO}_2/\text{M}_2\text{O}$  (however, M expresses alkali metal.) 1.5-2.6 it is -- a thing is used. the crystalline silicate used by JP,60-227895,A on the other hand --  $\text{SiO}_2 / \text{Na}_2\text{O}$  ratio (S/N ratio) 1.9-4.0 it is -- although -- this invention -- setting -- S/N ratio the silicate exceeding 2.6 -- a detergency -- falling -- 1.5 [ moreover, ] When it is the following, powder physical properties may fall and cautions are required.

[0069] What has the following presentation preferably as a crystalline silicate used for this invention is illustrated.  $x\text{M}_2\text{O} \cdot y\text{SiO}_2 \cdot z\text{MemOn} \cdot w\text{H}_2\text{O}$  (1) (it IIa(s) and IIb(s) M among a formula Ia group element of the periodic table, and Me) one sort or two sorts or more of combination chosen from IIIa, IVa, or a VIII group element -- being shown --  $y/x =$  -- it is 1.5-2.6,  $z/x = 0.01-1.0$ ,  $n/m = 0.5-2.0$ , and  $w = 0-20$ .  $x\text{M}_2\text{O} \cdot x'\text{SiO}_2 \cdot y'\text{H}_2\text{O}$  (2) (among a formula, M expresses alkali metal and is  $x' = 1.5-2.6$  and  $y' = 0-20$ .) The crystalline silicate of a presentation of the above-mentioned  $x'$  is explained first. In a general formula (1), M is chosen from Ia group element of the periodic table, and Na, K, etc. are mentioned as an Ia group element. these are independent -- it is -- for example,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  may be mixed and the  $\text{M}_2\text{O}$  component may be constituted. Me is chosen from IIa, IIb, IIIa, IVa, or the VIII group element of the periodic table, for example, Mg, calcium, Zn, Y, Ti, Zr, Fe, etc. are mentioned. Although especially these are not limited, they are Mg and calcium preferably from the point on a resource and insurance. moreover, these are independent -- it is -- two or more sorts may be mixed, for example,  $\text{MgO}$ ,  $\text{CaO}$ , etc. may be mixed, and the MemOn component may be constituted. Moreover, in the crystalline silicate in this invention, you may be a hydrate and the range of the amount of hydration in this case is  $w = 0-20$ .

[0070] Moreover, in a general formula,  $y/x$  is 1.5-2.6, and it is 1.5-2.2 preferably.  $y/x$  It has a bad influence on the powder physical properties of cleaning agent constituent constituents, such as caking nature, less than by 1.5. If  $y/x$  exceeds 2.6, a detergency will decline.  $z/x = 0.01-1.0$  -- it is -- desirable -- 0.02-0.9 it is . As for waterproof solubility, less than 0.01 are [  $z/x$  ] insufficient, and it is 1.0. If it exceeds, ion-exchange ability becomes low and is inadequate as an ion exchanger. If x, and y and z are relation as shown in aforementioned  $y/x$  and aforementioned  $z/x$ , they will not be limited especially. In addition, when  $x\text{M}_2\text{O}$  turns into  $x'\text{Na}_2\text{O} \cdot x'\text{K}_2\text{O}$  as mentioned above, x becomes  $x' + x$ . Such relation is  $z\text{MemOn}$ . Also in z in case a component consists of two or more sorts of things, it is the same. Moreover,  $n/m = 0.5-2.0$  The number of oxygen ion configured in the element concerned is shown, and it is 0.5, 1.0, 1.5, and 2.0 substantially. It is chosen out of a value.

[0071] The crystalline silicate of a presentation of  $x'$  in this invention is  $\text{M}_2\text{O}$ ,  $\text{SiO}_2$ , and MemOn, as shown in the aforementioned general formula. It consists of three components. Therefore, although each component is needed as the raw material in order to manufacture the crystalline silicate in this invention, a well-known compound is used suitably, without being limited especially in this invention. For example, an  $\text{M}_2\text{O}$  component and MemOn As a component, an independent or compound oxide, a hydroxide, salts, and the element content mineral concerned are used. [ of each ] [ of the element concerned ] Specifically as a raw material of an  $\text{M}_2\text{O}$  component,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ , and  $\text{Na}_2\text{SO}_4$  grade are MemOn. As a raw material of a component,  $\text{CaCO}_3$ , and  $\text{MgCO}_3$  and calcium  $(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ , a dolomite, etc. are mentioned.  $\text{SiO}_2$  As a component, a quartzite, a kaolin, talc, fused silica, silicate of soda, etc. are used.

[0072] the preparation approach of the crystalline silicate a presentation of  $x'$  in this invention serves as a value of x of the crystalline silicate made into the purpose, and y and z -- as -- the raw material component above-mentioned by the predetermined quantitative ratio -- mixing -- usually -- 300-1500 degrees C -- desirable -- 500-1000 degrees C -- further -- desirable -- The approach of calcinating and crystallizing in the range of 600 to 900 degree C is illustrated. In this case, heating temperature If crystallization of less than 300 degrees C is insufficient, it is inferior to waterproof solubility and 1500 degrees C is exceeded, a big and rough particle will be formed and ion-exchange ability will fall. Heating time is usual. It is 0.1 - 24 hours. Heating furnaces, such as an electric furnace and a gas furnace, can usually perform such baking.

[0073] the crystalline silicate of a presentation of  $x'$  in this invention -- as ion exchange capacity -- at least -- more than 100  $\text{CaCO}_3$  mg/g - - desirable -- It has 200 - 600  $\text{CaCO}_3$  mg/g.

[0074] Moreover, Si elution volume to water is  $\text{SiO}_2$ . It is usual by conversion. It is 110 or less mg/g and is substantially insoluble in water. in addition -- being substantially insoluble in water in this invention -- 2g of samples -- ion exchange water Si elution volume at the time of stirring [ be / it / under / 100g / adding ] at 25 degrees C for 30 minutes --  $\text{SiO}_2$  conversion -- usually -- Although things fewer than 110 mg/g are said, in this invention, the thing of 100 or less mg/g is more desirable, when fulfilling this effectiveness.

[0075] Next, the crystalline silicate of a presentation of the aforementioned  $x'$  is explained. This crystalline silicate General formula (2)  $\text{M}_2\text{O} \cdot x'\text{SiO}_2 \cdot y'\text{H}_2\text{O}$  (2) (among a formula, M expresses alkali metal and is  $x' = 1.5-2.6$  and  $y' = 0-20$ .) although it is what is expressed --  $x'$  in a general formula (2), and  $y'$  --  $1.7 \leq x' \leq$  -- the thing of 2.2 and  $y' = 0$  -- desirable -- cation-exchange ability It is one of the matter which can use the thing of 100 - 400  $\text{CaCO}_3$  mg/g, and has the ion prehension ability in this invention.

[0076] The process is indicated by JP,60-227895,A and, generally this crystalline silicate is vitrified silicate of soda of amorphism. It is obtained by calcinating at 200-1000 degrees C, and considering as crystallinity. the detail of a synthetic approach -- for example, -- Phys.Chem.Glasses. -- it is indicated by 7,127-138 (1966), Z.Kristallogr., 129, 396-404 (1969), etc. Moreover, this crystalline silicate can obtain powder and a granularity thing for example, from Hoechst A.G. as a trade name "Na-SKS -6" ( $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ ). in this invention, the crystalline silicate of a presentation of the aforementioned  $x'$  and  $y'$  is independent, respectively -- it is -- two or more sorts can be used together and used.

[0077] It is a process (2) if in charge of operation of this invention. It is desirable to add a surface coating agent between granulations thru/or after granulation, and to cover the front face of a detergent particle. The adhesion beyond the need between particles is lost by carrying out surface coating of the detergent particle. Mean particle diameter which between the granulations said here thru/or the granulation back pointed out the timing by which a detergent particle front face is covered with a surface coating agent, and the detergent particle made the purpose mostly 150-1500 micrometers Although it is a time of being corned at within the limits, some granulations may happen after addition.

[0078] As loadings of the surface coating agent for carrying out surface coating of the detergent particle in this invention, it is the detergent particle 100. 0.5 - 30 weight section is 1 - 25 weight section desirable still more preferably to the weight section. Moreover, for a surface coating agent, the mean particle diameter of a primary particle is 10 micrometers. It is desirable that they are the following pulverized coal. As this surface coating agent, since an aluminosilicate acts as a calcium ion scavenger at the time of wash, it is desirable, and especially the mean particle diameter of a primary particle is 10 micrometers. The following aluminosilicates are desirable. An aluminosilicate can also use crystallinity and amorphous any. The mean diameter of a primary particle is 10 micrometers in addition to an aluminosilicate. Non-subtlety fine particles like silicate compounds, such as the following silicon dioxides, a bentonite, talc, clay, and an amorphism silica derivative, are also desirable. As an example of silicate compounds, such as an aluminosilicate and an amorphism silica derivative, the



matter illustrated as an inorganic builder and porous oil absorption support is mentioned. Moreover, the mean particle diameter of a primary particle is 10 micrometers. The following metallic soap can be used similarly. the mean particle diameter of a primary particle -- 10 micrometers the approach by which the mean particle diameter of the following pulverized coal used light scattering, for example, a particle analyzer, (Horiba, Ltd. make) -- moreover, it is measured by measurement by microscope observation etc.

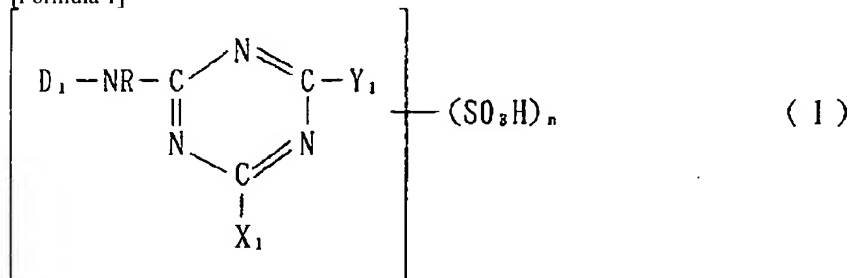
[0079] Moreover, it sets to this invention and is a process (3). It is a process (2) before performing compression for tablet-izing or briquette-izing. The acquired detergent particle or process (2) Solubility improves further by blending crystalline and water-soluble mineral salt with the detergent particle covered with the aforementioned surface coating agent behind. As mineral salt crystalline [ other than the silicate of this invention ], and water-soluble, although a carbonate, a sulfate, phosphate, etc. are mentioned, it is good to use more than a kind chosen from a carbonate and a sulfate especially in this invention. An alkali-metal salt is desirable also in these especially, and it is suitable to use potassium carbonate, a sodium sulfite, potassium sulfite, a potassium nitrate, a sodium chloride, and a sodium hydrogensulfate in this invention. Crystalline and water-soluble mineral salt is blended to a detergent particle by the weight ratio of / (mineral salt) (detergent particle or covering detergent particle) = 1 / 99 - 30/70. If this weight ratio is 1/99 or less, solubility will seldom change, and if it becomes 30/70 or more, solubility not only falls, but the degree of freedom of combination will be spoiled.

[0080] Moreover, mean particle diameter of 100-1500 micrometers By blending with a carbon number of six or less monochrome, polycarboxylic acid, or these salts, solubility becomes good more. As monochrome or polycarboxylic acid (salt), desirable things are an acetic acid (salt), a succinic acid (salt), a maleic acid (salt), and a citric acid (salt), and especially its sodium acetate and sodium citrate are desirable. With a carbon number of six or less monochrome or polycarboxylic acid (salt) is blended to a detergent particle by the weight ratio of [monochrome or polycarboxylic acid (salt)] / [detergent particle or covering detergent particle] = 1 / 99 - 30/70.

[0081] Furthermore, at this invention, it is a process (1). (2) It sets or is a process (3). The following additives can be used in front. (1) Bleaching agent fault sodium carbonate, sodium perborate, sodium-sulfate hydrogen-peroxide adduct (2), etc. Although hydrolases, hydases, oxidoreductases, desmolases, transferases, and isomerase will be mentioned if it classifies from the reactivity of an enzyme (it is enzyme which makes enzyme operation in washing process essentially.) enzyme, each is applicable to this invention. Especially desirable things are hydrolases and a protease, esterase, a carbohydrase, and nuclease are contained. The examples of a protease are a pepsin, a trypsin, a chymotrypsin, collagenase, keratinases, elastase, a SUPUCHI lysine, BPN, a papain, pro MERIN, carboxy peptidase A and B, amino peptidase, and the Asper GIROPEPU cytase A and B. The example of esterase has gust rucksack lipase, blowout rare tic lipase, vegetable lipase, phospholipases, choline esterase, and phospho TAZE. As an example of a carbohydrase, a cellulase, a maltase, saccharase, an amylase, a pectinase, a lysozyme, alpha-glycosidase, and beta-glycosidase are mentioned. (3) The blueing agent of blueing agent various kinds can also be blended if needed. For example, the following formula (I) And the object for \*\* of the thing of the structure of a formula (II) is carried out.

[0082]

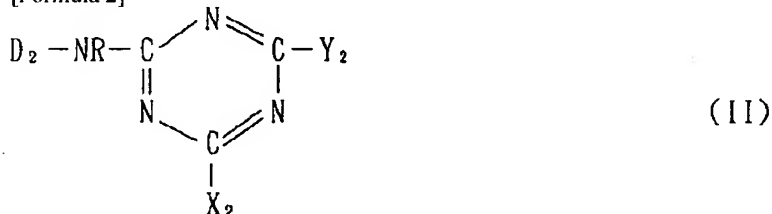
[Formula 1]



[0083] (Expressing monoazo blue [ D1 ] thru/ or purple, JISUAZO, or anthraquinone system coloring matter residue among a formula, that X1 and Y1 are also permuted by the hydroxyl-group; amino group, the hydroxyl group, the sulfonic group, the carboxylic-acid radical, or the alkoxy group and permuting by a certain aliphatic series amino-group; halogen atom, a hydroxyl group, the sulfonic group, the carboxylic-acid radical, the low-grade alkyl group, or the lower alkoxy group also express a certain aromatic series amino group or the annular aliphatic series amino group, and R expresses a hydrogen atom or a low-grade alkyl group.) However, R Except for the case where it is the case where a hydrogen atom is expressed, and either \*\*X1 and Y1 are hydroxyl groups at a list, and another side is an alkanol amino group when \*\*X1 and Y1 express a hydroxyl group or the alkanol amino group to coincidence. n expresses two or more integers.

[0084]

[Formula 2]



[0085] (Azo blue [ D2 ] thru/ or purple or anthraquinone system coloring matter residue is expressed among a formula.) R expresses a hydrogen atom or a low-grade alkyl group, and X2 and Y2 are the same -- or -- difference -- the alkanol amino group or a hydroxyl group is expressed. (4) A caking inhibitor Para toluenesulfonic acid salt, a xylene sulfonate, Acetate, sulfo succinate, talc, an impalpable powder silica, clay, calcium-silicate (for example, JohnsManvill microcell of a shrine etc.), Magnesium oxide (5) etc. The 3rd butylhydroxytoluene of an anti-oxidant, 4 and 4'-butylidenebis - (6-tertiary butyl-3-methyl phenol), 2 and 2'-butylidenebis - (6-tertiary butyl-4-methyl phenol), Mono-styrene-ized cresol, JISUCHIREN-ized cresol, a mono-styrene-ized phenol, A JISUCHIREN-ized phenol, 1, 1' anti-oxidant (6) fluorescent dye 4 and 4, such as -screw-(4-hydroxyphenyl) cyclohexane,-screw -(2-sulfo styryl)- Biphenyl salt, 4 and 4'-screw -(4-chloro-

3-sulfo styryl)- Biphenyl salt, One sort of a 2-(styryl phenyl) naphth thiazole derivative, 4, and 4'-screw (triazole-2-IRU) stilbene derivative and a bis(triazinylamino)stilbene disulfonate derivative or two sorts or more can be contained zero to 1% of the weight in a constituent. (7) It is one sort of a photoactivation bleaching agent sulfonation aluminum phthalocyanine and a sulfonation zinc phthalocyanine, or two sorts in a constituent 0-0.2 Weight % content of can be done. (8) Perfume (9) It is in a constituent about one sort, such as an anti-redeposition agent polyethylene glycol, polyvinyl alcohol, a polyvinyl pyrrolidone, and a carboxymethyl cellulose, or two sorts or more. It can contain 0.1 to 5%. (10) Although cationic surface active agents, such as amphoteric surface active agents, such as anionic surface active agents, such as surface-active-agent alkylbenzene sulfonates, alkyl or an alkenyl ethereal sulfate salt, alkyl or an alkenyl sulfate, an alpha olefin sulfonate, alpha-sulfo fatty-acid salt or an ester salt, alkyl or alkenyl ether carboxylate, and soap, carbobetaine, and sulfobetaine, and JI long-chain mold quarternary ammonium salt, etc. can be contained, it is desirable 3/4 of the weight of the Nonion activator and that it is 1/2 or less preferably. Since the bonding strength between the grain children exceeding three fourths becomes strong, the inclination for solubility to fall is shown.

[0086]

[Example] Although an example explains this invention to a detail below, this invention is not limited to these examples.

[0087] the example 1 of manufacture of examples 1-20 and the example 1 of a comparison - a 5 and a detergent particle - 4 [process (1) and (2)] REDIGE mixer (made in Matsusaka Research Institute --) the zeolite 4A mold of the presentation shown in Table 1 at path clearance 5.0mm of the capacity of 20l., an impeller, and a container wall, a sodium carbonate, and an amorphism aluminosilicate (0.8Na<sub>2</sub>O-aluminum<sub>2</sub>O<sub>3</sub> and 6.5SiO<sub>2</sub> --) Pore volume 3/100g, specific-surface-area 153m<sup>2</sup>/g, the oil absorption of 245ml / 100g, and the crystalline silicate (SKS-6, Hoechst A.G. make) of 310cm It supplies and is a main shaft (200rpm). Stirring of a chopper (4000rpm) was started. The Nonion activator 30 weight section was supplied there in 1 minute, and stirring after 4 minutes was stopped. Next, the zeolite 4A mold was thrown in as a surface lining agent, and it discharged by performing stirring for 30 seconds. In addition, the total charge was 4kg. Thus, bulk density of the obtained Nonion detergent particle and mean particle diameter It measures by the approach specified to JIS K 3362, and the bulk density and mean particle diameter are shown in Table 1.

[0088]

[Table 1]

			製造例 1	製造例 2	製造例 3	製造例 4	
配 合 成 分 (重 量 部)	ノニオン活性剤		30	40	50	30	
	ビルダー		ゼオライト4A型 (平均一次粒径 3 μm)	20	10	—	20
			炭酸ナトリウム (平均粒径 290 μm)	36	32	26	33
	結晶性シリケート*2		4	3	4	7	
	吸油剤	シリカ 誘導体	無定形アルミノ珪酸塩 (細孔容積: 310cm <sup>3</sup> /100g 比表面積: 153m <sup>2</sup> /g 吸油量 : 245ml/100g)	10	15	20	10
	表面被膜剤		ゼオライト4A型 (平均一次粒径 3 μm)	15	15	15	—
洗 剤 粒 子			嵩 密 度 (g/ml)	0.85	0.84	0.86	0.71
			平均粒径 (μm)	420	370	450	260

\*1: エチレンオキサイド平均付加モル数=8、融点15°C

\*2: ヘキスト社製 SKS-6

[0089] - Spray drying of the slurry of 50 % of the weight of moisture of each component for spray drying particles shown in the example 5-8 [process (1) and process (2)] table 2 of manufacture of a detergent particle was carried out, and the spray drying particle was obtained. The obtained spray drying particle, the zeolite 4A mold of the amount shown in Table 2, and an amorphism aluminosilicate (0.8Na<sub>2</sub>O-aluminum<sub>2</sub>O<sub>3</sub> and 6.5SiO<sub>2</sub>), The sodium carbonate and the crystalline silicate (except for SKS-6, the Hoechst A.G. make, and the example 8 of manufacture) were fed into the REDIGE mixer (path clearance of made in Matsusaka Research Institute, the capacity of 20l., an impeller, and a container wall 5.0mm), and stirring of a main shaft (200rpm) and a chopper (4000rpm) was started. The Nonion activator of the amount shown in Table 2 was thrown in there in 1 minute, and stirring after 4 minutes was stopped. Next, the zeolite 4A mold was thrown in as a surface lining agent, and it discharged by performing stirring for 30 seconds. In addition, a total preparation capacity was 4kg. Thus, it measures by the approach to which the bulk density of the obtained Nonion detergent particle and mean particle diameter were specified at JIS K 3362, and the result is shown in Table 2. In addition, the example 8 of manufacture is an example of comparison manufacture.

[0090]

[Table 2]

			製造例 5	製造例 6	製造例 7	製造例 8	
配 合 成 分 (重量部)	ノニオン活性剤		ポリオキシエチレン ドデシルエーテル*1	15	15	30	15
	ビルダー		ゼオライト 4 A 型 (平均一次粒径 3 μm)	25	25	20	25
			炭酸ナトリウム (平均粒径 290 μm)	20	20	10	40
			結晶性ケイ酸塩 *2	20	20	10	—
	吸油剤	噴霧乾燥粒子	ゼオライト 4 A 型	13.9	12.9	13.9	12.9
			炭酸ナトリウム	5.0	5.0	5.0	5.0
			脂肪酸ナトリウム (平均炭素数18)	—	1.0	—	1.0
			CMC - Na *3	0.1	0.1	0.1	0.1
			水分	1.0	1.0	1.0	1.0
			嵩 密 度 (g/ml)	0.70	0.43	0.70	0.43
			平均 粒 径 (μm)	210	220	210	220
		シリカ誘導体	無定形アルミノ珪酸塩 (細孔容積 : 310cm <sup>3</sup> /100g 比表面積 : 153m <sup>2</sup> /g 吸油量 : 245ml/100g)	—	—	10	—
	表面被膜剤		ゼオライト4A型 (平均一次粒径 3 μm)	15	15	15	15
	洗 剤 粒 子		嵩 密 度 (g/ml)	0.84	0.75	0.83	0.73
平均 粒 径 (μm)			410	430	435	430	

\*1 : エチレンオキサイド平均付加モル数 = 8、融点15°C

\*2 : ヘキスト社製、SKS-6

\*3 : カルボキシルメチルセルロースナトリウム塩

[0091] It mixed at a rate which shows the mineral salt shown in the Nonion detergent particle obtained in the examples 1-8 of manufacture, and Tables 3-4, or carboxylate in Tables 3-4, and the detergent particle was obtained.

[0092] (Process 3) the detergent particle obtained above by the briquetting machine (BSS[ by Sintokogio, Ltd. ]- 501 mold) -- supplying -- height 3.1mm and path 4.8mm -- [ -- the briquette mentioned to JIS Z 8841, description, and Table 1 "the configuration of a granulation object, and a name" -- it is -- a shaft-orientations perpendicular projection image almond form, the circle of path 4.8 mm (average), and the diameter direction thickness [ ] -- it is thickness 0.2 mm by central path clearance in 3.1mm. ] Degree of consolidation 1.7 to the bulk density of the detergent particle before processing The ellipse ball-shaped briquette was obtained. The service condition of a briquetting machine is roll rotational frequency 30rpm and the amount of detergent particle feed. 100 kg/hr, roller clearance 0.2mm and the opening-of-sieve aperture for trimming are an upper case. It is 7.4mm and 2.38mm of lower berths, and what passed through the upper case and did not pass the lower berth was used as the final product. However, the detergent particle of the example 8 of manufacture is 50 kgf/cm<sup>2</sup>. It is a pressure and considered as 10mm in 3cm of diameters, and thickness, and the tablet of the cylindrical shape of mass 7.5 g per piece. Thus, the ease of scattering of the powder of the obtained briquette mold detergent was viewed and judged, and the following conditions estimated solubility. The result is shown in Tables 3-4.

[0093] 15g of briquette mold detergents obtained by the <soluble test-method> above is fed into 2 tub type washing machine (Toshiba) into which tap water (20 degrees C and 30l.) was put beforehand. Electrical conductivity was measured stirring for 15 minutes by making stirring reinforcement into a "criterion." The used measurement machine of electrical conductivity is the Toa Electronics, Ltd. make (TOA Conductivity Meter CM-60S). Change of the electrical conductivity after after [ stirring ] 5-minute progress made the saturation value (terminal point) of electrical conductivity the value which is less than 1%. And it asked for the rate of the dissolution from the following formula.

[0094]

[Equation 1]

$$\text{溶解率} = \frac{\left( \frac{\text{ある時間での洗濯液の電気伝導度}}{\text{洗濯液の電気伝導度の飽和値}} \right) - \left( \frac{\text{洗剤投入前の水の電気伝導度}}{\text{電気伝導度}} \right)}{\left( \frac{\text{洗濯液の電気伝導度の飽和値}}{\text{電気伝導度}} \right) - \left( \frac{\text{洗剤投入前の水の電気伝導度}}{\text{電気伝導度}} \right)} \times 100$$

[0095] The time amount from which the above-mentioned rate of the dissolution becomes 90% estimated solubility. Although the result is shown in Tables 3-4, in the exam approach, it is desirable that the time amount from which the rate of the dissolution becomes 90% is 5 or less minutes.

[0096]

[Table 3]

			実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	実施例 6	実施例 7	実施例 8	実施例 9	実施例 10	実施例 11
配 合 成 分 (重 量 %)	ノニオン 洗剤粒子	製造例 1	100	85	85	85	80						
		製造例 2						85			99.5	60	
		製造例 3							85				
		製造例 4								85			80
	無機酸 又は カルボン 酸塩	炭酸ナトリウム 平均粒径=350 μm		15			5						
		炭酸カリウム 平均粒径=200 μm			15			15			0.5	40	20
		酢酸ナトリウム 平均粒径=350 μm				15			15				
		クエン酸ナトリウム 平均粒径=300 μm					15			15			
評価結果	溶解性 (分)		5	5	3	3	4	4	4	4	5	4	3
	粉の飛び散り		無し	無し	無し	無し	無し	無し	無し	無し	無し	無し	無し

[0097]

[Table 4]

			実 施 例										比較品
			12	13	14	15	16	17	18	19	20	21	1
配 合 成 分 (重 量 %)	ノニオン 洗剤粒子	製造例 5	100	85	85	85	80					80	
		製造例 6						85		99.5	60		
		製造例 7							85				
		製造例 8											99.5
	無機酸 又は カルボン 酸塩	炭酸ナトリウム 平均粒径=350 μm		15			5						
		炭酸カリウム 平均粒径=200 μm			15			15		0.5	40	20	0.5
		酢酸ナトリウム 平均粒径=350 μm				15			15				
		クエン酸ナトリウム 平均粒径=300 μm					15						
評価結果	溶解性 (分)		4	4	4	3	4	3	3	5	5	5	12
	粉の飛び散り		無し	無し	無し	無し	無し	無し	無し	無し	無し	無し	無し

[0098] (Note)

Example 21: Detergent particle which added and obtained potassium carbonate to the detergent particle of the example 5 of manufacture 50 kgf/cm<sup>2</sup> What was prepared by the pressure in the tablet mold detergent with 10mm [ in 3cm of diameters, and thickness ], and a mass of 15g.

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[Translation done.]